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The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

⑳ **Substituted aryl or heteroaryl diones.**

㉑ Compounds of the general formula



wherein

A is a cyclic 1-one-2-ene-3-ol-2-yl residue;

B is an aryl or heteroaryl group bearing at least one hydrocarbyl substituent attached via an -OSO₂- or -NSO₂- bridge and optionally bearing further substituents; and salts, enolethers and enolesters thereof, and methods of producing such compounds and using such compounds as herbicides and acaricides are disclosed.

Description

IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOUNDS

This invention relates to novel substituted aryl or heteroaryl diones and related compounds, intermediates therefor, synthesis thereof, and the use of said compounds for the control of weeds and acari.

- 5 Cyclic 1-one-2-ene-3-ol compounds substituted in the 2-position by an aroyl or heteroaroaryl group and enol ethers and enol esters thereof are known herbicidal compounds. It has been found that 2-aroyl and 2-heteroaroaryl-(cyclic 1-one-2-ene-3-ol) compounds, wherein the aroyl or heteroaroaryl group bears a hydrocarbylsulfonyloxy and/or a hydrocarbylsulfonylamino substituent, as well as enol ethers and enolesters thereof have interesting biological properties. They are indicated for agricultural use, in particular for the control of undesired vegetation.

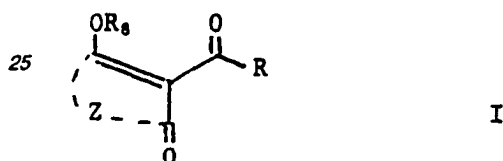
10 More particularly, this invention concerns compounds of the general formula



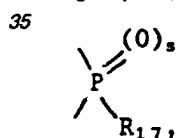
- 15 A is a cyclic 1-one-2-ene-3-ol-2-yl residue;
B is an aryl or heteroaryl group bearing at least one hydrocarbyl substituent attached via an -OSO₂- or -NSO₂- bridge and optionally bearing further substituents; and salts, enolethers and enolesters thereof.

- The term hydrocarbyl as used herein stands for unsubstituted or substituted hydrocarbyl. The hydrocarbyl group conveniently contains from one to eight carbon atoms and may be straight or branched, saturated or unsaturated, comprise or consist of a ring which may be saturated, unsaturated or aromatic. Examples of suitable hydrocarbyl substituents are apparent from the definition of R₁₂ hereinafter.

A particular group of compounds is that represented by formula I



- 30 wherein
Z is a C₂-C₁₀ alkylene group, optionally substituted with one or more members selected from C₁-alkyl, C₁-alkoxy, C₁-alkylthio, COOR₁₆, halogen, cyano; nitro; phenyl; R₉SO_n'; benzyl; -NR₁₀R₁₁; R₁₂C(O)-; -SO₂NR₁₀R₁₁; and -N(R₁₀)C(O)R₁₁; said Z group further being optionally interposed by an oxygen atom, a group -S(O)_p-, a group



- 40 or a group -N(R₁₆)-; and whereby two of any alkyl substituents may be joined to form a bicyclic, spiro or bridged alkylene ring;

- R is phenyl or a 5- or 6-membered aromatic heterocycle containing one or two heteroatoms selected from oxygen, sulfur, and nitrogen; R being substituted by at least one member selected from the group consisting of -OSO₂R₁₂ and -NR₁₅SO₂R₁₂; R being optionally further substituted by one or two members selected from C₁-alkyl, optionally substituted with one to six halogen atoms; C₁-alkoxy, optionally substituted with one to six halogen atoms; phenyl; halogen; cyano; nitro; -(O)_nS(O)_nR₉'; -SO₂NR₁₀R₁₁'; -N(R₁₀')C(O)R₁₁'; or -NR₁₅'SO₂R₁₂'; whereby any two adjacent alkyl substituents may be joined to form a bicyclic alkylene ring; R₈ is hydrogen; C₁-alkyl; C₁-alkylcarbonyl; C₁-alkoxycarbonyl; C₁-alkylsulfonyl; C(O)NR₁₃R₁₄; P(O)(OR₁₁)₂; R₁₃P(O)OR₁₁; or salt forming moiety.

- 50 R₉ and R₉' are independently phenyl; benzyl; or C₁-alkyl, optionally substituted by one or more members selected from halogen, cyano, C₁-alkoxy or C₁-alkylthio;

R₁₀, R₁₀', R₁₁, R₁₁', R₁₁'', R₁₃, R₁₄, R₁₅, R₁₅', and R₁₆ are independently hydrogen C₁-alkyl;

- 55 R₁₂ and R₁₂' are independently C₁-alkyl, optionally substituted with one to six halogen atoms; or phenyl, optionally substituted with one to three members selected from C₁-alkyl, C₁-alkylcarbonyl, C₁-alkoxycarbonyl, C₁-alkylsulfonyl, C(O)NR₁₃R₁₄, P(O)(OR₁₁')₂ and R₁₃P(O)OR₁₁';

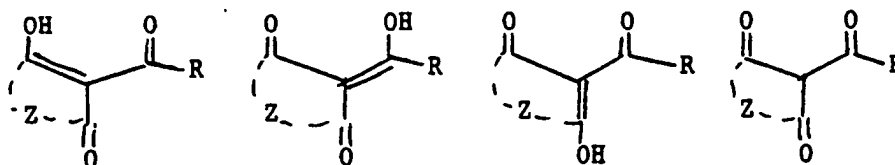
R₁₇ is C₁-alkyl or C₁-alkoxy;

R₁₈ is C₁-alkyl;

n' and p are independently 0, 1 or 2; and

- 60 n and s are independently 0 or 1.

Enol compounds of the formula (I), wherein R₈ is H, can exist in a number of tautomeric forms, the following being representative:



It is intended that all such tautomeric structures are included within the scope of this invention.

In preferred compounds of formula I, Z is an unsubstituted or substituted C₂₋₃ alkylene group. Where Z is substituted by C₁₋₈alkyl, it is preferably substituted by C₁₋₄alkyl.

Where Z is substituted by C₁₋₈alkoxy, it is preferably substituted by C₁₋₄alkoxy.

Where Z is substituted by C₁₋₈alkylthio, it is preferably substituted by C₁₋₄alkylthio.

Where Z is substituted by halogen, it is preferably bromo, chloro, or fluoro.

Where any two alkyl substituents of Z are joined to form a bicyclic, spiro or bridged alkylene ring, such alkylene ring preferably has one to five carbons.

Preferred substituents of Z are C₁₋₄alkyl, SC₁₋₄alkyl, and SO₂C₁₋₄alkyl.

Where Z is interposed, it is preferably interposed by an oxygen or sulfur atom.

Where R is an aromatic heterocycle, it is, e.g., a thienyl, pyrazolyl, pyridyl or pyrimidinyl, preferably a pyrimidinyl ring.

R is preferably substituted phenyl.

Where R is further substituted, it is preferably further substituted by one or two substituents, those substituents being selected from C₁₋₄alkyl, C₁₋₄alkoxy, NO₂, bromo, chloro and fluoro.

Where any two alkyl substituents of R are joined to form a bicyclic alkylene ring, such alkylene ring preferably has three to four carbon atoms.

Where any of R₈, R₉, R₉', R₁₀, R₁₀', R₁₁, R₁₁', R₁₁'', R₁₃, R₁₄, R₁₅, R₁₆, R₁₂, R₁₂', R₁₇, and R₁₈ is or contains alkyl, it is preferably C₁₋₄alkyl.

Where any of R₈, R₁₂, R₁₂', R₁₃, R₁₇ is or contains alkoxy, it is preferably C₁₋₄alkoxy.

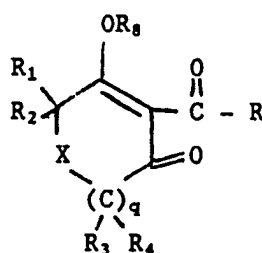
R₈ is preferably hydrogen, C₁₋₄alkyl, C₄₋₈alkylcarbonyl, benzoyl, or C₁₋₄alkylsulfonyl, more preferably hydrogen, methyl, ethyl, t-butylcarbonyl, isobutylcarbonyl, benzoyl or methylsulfonyl.

Where R₈ is a salt forming moiety, it is preferably inorganic e.g. a metal equivalent of Na, Ca, Fe or Cu; or organic, e.g., the ammonium salt moiety of an amine (such as 1-(methylaminomethyl)-naphthalene), a sulfonium, sulfoxonium or phosphonium moiety. Depending on the nature of R₈, the salt may exist in chelated form.

R₁₂ is preferably phenyl or C₁₋₄alkyl, optionally substituted with one to three halogen atoms; more preferably phenyl or C₁₋₃alkyl, optionally substituted with one or three bromo, chloro, or fluoro atoms.

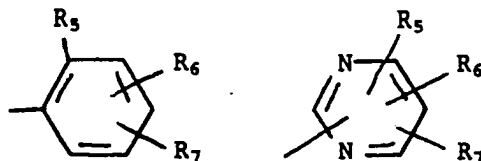
R₁₅ is preferably hydrogen or C₁₋₄alkyl, more preferably hydrogen.

A particular subgroup of compounds of formula I is that represented by formula Ia



wherein,

R is selected from the groups



X is oxygen, S(O)_n, CR₁'R₂' or NR₁₈;

R₁, R₁', R₂, R₂', R₃, and R₄ are independently, hydrogen, C₁₋₈alkyl, C₁₋₈alkoxy, C₁₋₈alkylthio, or COOR₁₆; or R₁ and R₂ together form a C₃₋₈alkylene; or R₂ and R₂' together form a C₂₋₄alkylene optionally substituted with one to six C₁₋₈alkyl groups; or R₃ and R₄ together form a C₃₋₈alkylene;

R₅ is C₁₋₈alkyl, optionally substituted with one to six halogen atoms; C₁₋₈alkoxy, optionally substituted with one to six halogen atoms; -(O)_nS(O)_nR₁₂; -NR₁₅SO₂R₁₂; halogen; cyano; or nitro;

each of R₆ and R₇ is independently hydrogen or selected from the values of R₅; with the proviso that at least one of R₅, R₆, and R₇ is a group -OSO₂R₁₂ or -NR₁₅SO₂R₁₂;

R₈, R₁₂, R₁₅, R₁₆, R₁₈, n, and n' are as previously defined; and q is 0 or 1.

In preferred compounds of formula Ia, X is oxygen, sulfur or CR₁', R₂', more preferably CR₁'R₂'. R is preferably substituted phenyl.

5 Where any of the substituents R₅-R₇ and R₁₂ is or contains halogen, such halogen is preferably selected from bromo, chloro, and fluoro.

Where any of R₁, R₁', R₂, R₂', R₃, R₄, R₅, R₆, R₇, R₈, R₁₂-R₁₆, and R₁₈ is or contains alkyl, it is preferably of one to four carbons.

10 Where R₁ and R₂, R₂ and R₂', or R₃ and R₄ together form an alkylene, it is preferably of two to five carbon atoms.

Where any of R₅-R₈ are or contains C₁₋₈alkoxy, it is preferably of one to four carbons.

Each of R₁, R₁', R₂, R₂', R₃, and R₄ is preferably hydrogen or C₁₋₄alkyl; such alkyl is more preferably of one to three carbons.

15 R₅ is preferably -(O)_nS(O)_nC₁₋₄alkyl, halogen, nitro or C₁₋₄alkyl optionally substituted with halogen, more preferably methyl, CF₃, C₁₋₃alkylsulfonyl, C₁₋₃alkylsulfonyloxy, chloro, bromo or nitro, still more preferably nitro.

R₆ is preferably hydrogen, C₁₋₄alkyl; C₁₋₄alkoxy, C₁₋₃alkylsulfonyloxy, bromo, or chloro. R₈ is more preferably hydrogen, methoxy, methylsulfonyloxy or chloro, still more preferably hydrogen.

20 R₇ is preferably bromo, chloro, OSO₂C₁₋₄alkyl, OSO₂C₁₋₄haloalkyl, OSO₂phenyl or NR₁₅SO₂C₁₋₄alkyl. R₇ is more preferably chloro, OSO₂phenyl or C₁₋₃alkylsulfonyloxy, still more preferably C₁₋₂alkylsulfonyloxy.

R₈ is preferably hydrogen, C₁₋₄alkyl, C₄₋₈alkylcarbonyl, benzoyl, or C₁₋₄alkylsulfonyl. R₈ is preferably hydrogen, methyl, ethyl, t-butylcarbonyl, isobutylcarbonyl, benzoyl or methylsulfonyl.

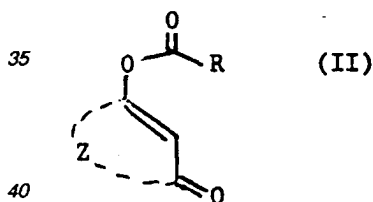
R₁₂ is preferably phenyl or C₁₋₄alkyl, optionally substituted with one to three halogen atoms; more preferably phenyl or C₁₋₃alkyl, optionally substituted with one to three bromo, chloro, or fluoro atoms.

25 R₁₅ is preferably H or C₁₋₄alkyl, more preferably H. q is preferably 1.

Preferably R₆ is in the 3-position and R₇ is in the 4-position. In the description and claims hereinafter, each of R-R₁₈, X, Z, n, n', q, p, and s is as defined above, unless otherwise specified.

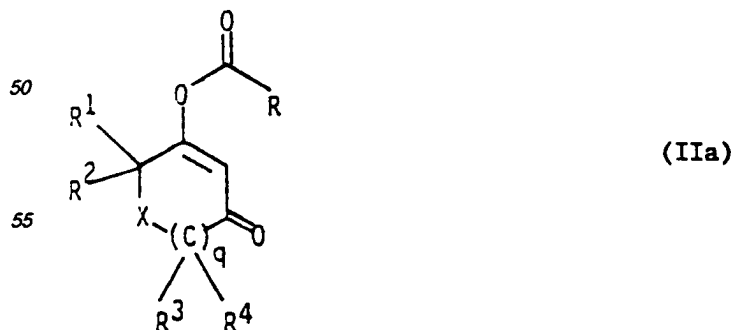
30 The compounds of the present invention of formula I are new substances which can be prepared by methods analogous to methods known in the art for the preparation of 2-aroxy-(cyclic-1,3-diones) and enol ethers or enol esters thereof.

More particularly, they can be obtained by, for example: reacting an enol ester of formula (II)



wherein R and Z are as defined above, with a cyanide source and a moderate base to give a compound of formula I where R₈ is hydrogen, followed, where desired, by etherification or esterification to the corresponding enol ethers or enol esters.

45 Similarly, the compounds of formula Ia can be obtained by, for example: reacting an enol ester of formula (IIa)



wherein R, X, q, t and R₁-R₄ are as defined above, with a cyanide source and a moderate base to obtain a compound of formula Ia where R₈ is hydrogen, followed, where desired, by etherification or esterification to the corresponding enol ethers or enol esters.

65 The above reaction is carried out in the presence of a catalytic amount of source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base. The

reaction is conveniently carried out in a solvent which is inert under the reaction conditions, e.g. 1,2-dichloroethane, toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide (DMF) and methyl isobutyl ketone (MIBK). In general, depending on the nature of the reactants and the cyanide source, the rearrangement may be conducted at temperatures up to about 80°C. In some cases, for instance when there is a possible problem of excessive by-product formation, the temperatures should be kept at about 40°C maximum.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1-4 carbon atoms in the alkyl groups, such as acetone or methyl isobutyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C₂-C₆ aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin. The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. Generally about 1-10 mole % of the cyanide source is preferred.

By the term "moderate base" is meant a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this reaction include both organic bases such as tertiary amines and inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines include trialkylamines such as triethylamine, trialkanolamines such as triethanolamine, and pyridine. Suitable inorganic bases include potassium carbonate and trisodium phosphate. The base is used in an amount of from about 1 to about 4 moles per mole of enol ester, preferably about 1.3-2 moles per mole.

When the cyanide source is an alkali metal cyanide, particularly potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.

Depending on the reaction conditions, the thus obtained keto-enol compounds may be in free acid form (R₈ is H) or in salt form; where they are in salt form (i.e. R₈ is a salt forming moiety), R₈ may be inorganic (e.g. a metal equivalent of Na, Ca, Fe or Cu) or organic, e.g. the ammonium salt moiety of an amine, sulfonium, sulfoxonium or phosphonium moiety. Depending on the nature of R₈, the salt may exist in chelated form. The salt form may be converted to the corresponding acid form (R₈ is H) in a manner known per se, and vice versa.

Compounds of formula I where R₈ is other than hydrogen or a salt forming moiety can be prepared in a manner known per se for the preparation of enol ethers or enol esters from the corresponding enol compounds, e.g. by reacting a compound of formula I where R₈ = H with either

a) the group R₈-OH and a catalyst, or

b) the group R₈-Q and a moderate base, wherein Q is a halogen atom, to give a compound of formula I where R₈ is as defined above other than hydrogen or a salt forming moiety.

The above reaction a) is carried out in the presence of a catalyst such as concentrated sulfuric acid. The reaction is conveniently carried out in a solvent which is also the reactant such as methano, and at an elevated temperature.

The above reaction b) is carried out in the presence of a moderate base such as triethylamine or pyridine and conveniently at RT or below.

The compounds of formula I may be recovered from the reaction mixture in which they are formed by working up by established procedures.

The starting materials and reagents employed in the process described herein are either known or, insofar as they are not known, may be produced in a manner analogous to the processes described herein or to known processes.

The novel compounds of formula I are useful for the control of weeds, using pre- and/or post-emergent treatments. Some of them are also useful as plant regulators and as acaricides. Application of a compound of the present invention as a herbicide is made according to conventional procedure to the weeds or their locus using an herbicidally effective amount of the compounds, usually from about one-half or less to ten pounds per acre.

Application of a compound of the present invention as an acaricide is made according to conventional procedure to the spite of acarici infestation using an acaricidally effective amount of the compounds, usually 100 g/ha to 1 kg/ha.

The term "herbicide", as used herein, refers to an active ingredient which modifies the growth of plants because of phytotoxic or plant growth regulating properties so as to retard the growth of the plant or damage the plant sufficiently to kill it.

The compounds of the present invention, when applied as either post or pre-emergents, demonstrate high levels of herbicidal activity on broadleaf, grass and sedge weeds.

In the use of the compounds of formula I as a herbicide or acaricide, a compound of formula I, or mixtures thereof, can conveniently be employed as agricultural compositions in association with acceptable diluent(s) for application to the weed, acari, or their loci. Such compositions also form part of the present invention.

Methods of preparing suitable compositions which can be used with a compound of the present invention are described in the literature along with suitable liquid and solid carriers. The optimum usage of a compound of the present invention is readily determinable by one of ordinary skill in the art using routine testing such as greenhouse testing and small plot testing.

Suitable compositions contain from 0.01 to 99 % by weight of active ingredient, from 0 to 20 % of surfactant

and from 1 to 99.99 % of solid or liquid diluent(s). Higher ratios of surfactant to active ingredient are sometimes desirable and are achieved by incorporation into the formulation or by tank mixing. Application forms of a composition generally contain between 0.01 and 25 % by weight of active ingredient. Lower or higher levels of active ingredient can, of course, be present depending on the intended use, the physical properties of the compound and the mode of application. Concentrate forms of a composition intended to be diluted before use generally contain between 2 and 90 %, preferably between 5 and 81 % by weight of active ingredient.

Useful compositions containing the compound of formula I include dusts, granules, suspension concentrates, wettable powders, flowables and the like. They are obtained by conventional manner, e.g. by mixing a compound of formula I with the diluent(s) and optionally with other ingredients.

EXAMPLE A

Preparation of a Dust

10 Parts of a compound according to this invention and 90 parts of powdered talc are mixed in a mechanical grinder-blender and are ground until a homogeneous, free-flowing dust of the desired particle size is obtained. This dust is suitable for direct application to the site of the weed, acari infestation.

EXAMPLE B

Preparation of Wettable Powder

25 Parts of a compound according to this invention are mixed and milled with 25 parts of synthetic fine silica, 2 parts of sodium lauryl sulphate, 3 parts of sodium ligninsulphonate and 45 parts of finely divided kaolin until the mean particle size is about 5 micron. The resulting wettable powder is diluted with water before use to a spray liquor with the desired concentration.

EXAMPLE C

Preparation of Emulsifiable Concentrate (EC)

13.37 Parts of a compound according to this invention are mixed in a beaker with 7.04 parts of Toximul 360A (a mixture of anionic and non-ionic surfactants containing largely anionic surfactants), 23.79 parts of dimethylformamide and 55.8 parts of Tenneco 500-100 (predominantly a mixture of alkylated aromatics such as xylene and ethylbenzene) until solution is effected. The resulting EC is diluted with water for use.

Alternatively, the compounds of formula I may be used in micro-encapsulated form.

The compounds of formula I can be combined with a cyclodextrin to make a cyclodextrin inclusion complex for application to the pest or its locus.

Agriculturally acceptable additives may be employed in the compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion, for example.

"Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin sulfonate and lauryl sulfate.

"Diluent" as used herein means a liquid or solid agriculturally acceptable material used to dilute a concentrated material to a usable or desirable strength. For dusts or granules it can be e.g. talc, kaolin or diatomaceous earth, for liquid concentrate forms for example a hydrocarbon such as xylene or an alcohol such as isopropanol, and for liquid application forms e.g. water or diesel oil.

The compositions of this invention can also comprise other compounds having biological activity, e.g. compounds having similar or complementary herbicidal activity for broadspectrum weed control or compounds having complimentary acaricidal activity or compounds having antidotal, fungicidal, insecticidal or insect attractant activity.

The following examples are provided to illustrate the practice of the present invention. Temperature is given in degrees Centigrade. RT means room temperature. Parts and percentages are by weight.

PREPARATION OF FINAL COMPOUNDS

EXAMPLE 1

To a solution of 2,2,6,6-tetramethyl-5-(3-methoxy-4-methylsulfonyloxy-2-nitrobenzoyloxy)-3,6-dihydro-2H-pyran-3-one (7.80 g) in 50 ml of acetonitrile are added triethylamine (4.91 ml, 2 eq.) and acetone cyanohydrin (1.0 ml) in one portion. The mixture is stirred at RT overnight, after which it is diluted with water and extracted with ether. The ether is removed and the residue is purified by PTLC to give 2,2,6,6-tetramethyl-4-(3-methoxy-4-methylsulfonyloxy-2-nitrobenzoyl)-2H-pyran-3,5-(4H,6H)-dione (compound 1, Table A).

EXAMPLE 2

To a solution of 5-methyl-1-(4-methylsulfonyloxy-2-chlorobenzoyloxy)-1-cyclohexene-3-one (5.30 g) in 25 ml of acetonitrile are added triethylamine (3.97 ml, 2 eq.) and acetone cyanohydrin (0.4 ml), and the mixture is

stirred at RT overnight. The acetonitrile is removed, and the residue is taken up in water and extracted with methylene chloride. The combined organic extracts are washed with dilute HCl and with brine, dried and evaporated to dryness. The crude product is crystallized from ether to give 5-methyl-2-(4-methylsulfonyloxy-2-chlorobenzoyl)-cyclohexane-1,3-dione (compound 32, Table A).

EXAMPLE 3

Following the procedure of Examples 1 and 2, each of the compound under Table A is prepared by rearrangement of the corresponding enol ester.

EXAMPLE 4

A solution of 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-2H-pyran-3,5-(4H,6H)-dione (2.54 mmol) and 2 drops of conc. sulfuric acid in 20 ml of methanol is heated under reflux for 48 hours. The reaction mixture is concentrated and the residue is taken up in ether. The ethereal solution is washed with aqueous sodium bicarbonate and with brine, dried and evaporated to dryness to give 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-5-methoxy-3,6-dihydro-2H-pyran-3-one.

EXAMPLE 5

To a mixture of 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-2H-pyran-3,5-(4H,6H)-dione (2.26 mmol) in methylene chloride (10 ml) containing triethylamine (0.47 ml, 3.39 mmol) is added dropwise at 0° a solution of acetyl chloride (0.27 g, 3.39 mmol) in 5 ml of methylene chloride. The resulting mixture is stirred for 30 min., and is then diluted with methylene chloride, washed, dried and evaporated to dryness to give 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-5-acetoxy-3,6-dihydro-2H-pyran-3-one.

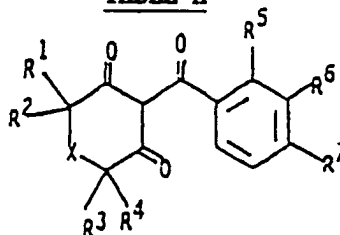
EXAMPLE 6

Following the procedure of Example 5, the final compounds under column I are prepared by the reaction of 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-2H-pyran-3,5-(4H,6H)-dione with the corresponding acyl chloride.

I

- | | | |
|-----|---|--|
| 26. | 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-5-propionyloxy-3,6-dihydro-2H-pyran-3-one | |
| 27. | 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-5-isobutyryloxy-3,6-dihydro-2H-pyran-3-one | |
| 28. | 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-5-pivaloyloxy-3,6-dihydro-2H-pyran-3-one | |
| 29. | 2,2,6,6-tetramethyl-4-(4-methylsulfonyloxy-2-nitrobenzoyl)-5-benzoyloxy-3,6-dihydro-2H-pyran-3-one | |

TABLE A



Cpd	X	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	m. p. (°C)
1	0	CH ₃	CH ₃	CH ₃	CH ₃	NO ₂	OCH ₃	OSO ₂ CH ₃	114
2	0	CH ₃	CH ₃	CH ₃	CH ₃	NO ₂	H	OSO ₂ CH ₃	
3	0	CH ₃	CH ₃	CH ₃	CH ₃	Cl	H	OSO ₂ CH ₃	112
4	0	CH ₃	CH ₃	H	H	NO ₂	H	OSO ₂ CH ₃	
5	0	CH ₃	CH ₃	H	H	Cl	H	OSO ₂ CH ₃	
6	0	CH ₃	CH ₃	H	H	Cl	Cl	OSO ₂ CH ₃	
7	0	CH ₃	CH ₃	H	H	CH ₃	H	OSO ₂ CH ₃	
8	0	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	H	OSO ₂ CH ₃	
9	0	CH ₃	CH ₃	CH ₃	CH ₃	Cl	Cl	OSO ₂ CH ₃	
10	0	CH ₃	H	CH ₃	H	Cl	Cl	OSO ₂ CH ₃	
11	0	CH ₃	H	CH ₃	H	Cl	H	OSO ₂ CH ₃	99
12	0	CH ₃	H	CH ₃	H	CH ₃	H	OSO ₂ CH ₃	
13	0	CH ₃	H	CH ₃	H	NO ₂	H	OSO ₂ CH ₃	
14	0	CH ₃	H	CH ₃	H	NO ₂	OCH ₃	OSO ₂ CH ₃	
15	0	CH ₃	H	CH ₂ CH ₃	H	NO ₂	H	OSO ₂ CH ₃	83.5-86
16	0	CH ₃	H	CH ₂ CH ₃	H	Cl	H	OSO ₂ CH ₃	oil
17	0	CH ₃	H	CH ₃	H	CH ₃	H	OSO ₂ CH ₃	
18	0	CH ₃	CH ₃	CH ₃	CH ₃	NO ₂	H	OSO ₂ CH ₂ Cl	
19	0	CH ₃	CH ₃	CH ₃	CH ₃	Cl	H	OSO ₂ CH ₂ Cl	
20	0	CH ₃	CH ₃	CH ₃	CH ₃	CH ₃	H	OSO ₂ CH ₂ Cl	
21	0	CH ₃	H	CH ₃	H	NO ₂	H	OSO ₂ CH ₂ Cl	
22	0	CH ₃	H	CH ₃	H	Cl	H	OSO ₂ CH ₂ Cl	
23	0	CH ₃	CH ₃	CH ₃	CH ₃	OSO ₂ CH ₃	H	Cl	
24	0	CH ₃	CH ₃	CH ₃	CH ₃	OSO ₂ CH ₃	H	Br	
25	0	CH ₃	H	CH ₃	H	OSO ₂ CH ₃	H	Cl	
26	0	CH ₃	CH ₃	CH ₃	CH ₃	Cl	OSO ₂ CH ₃	Cl	
27	0	CH ₃	H	CH ₃	H	Cl	OSO ₂ CH ₃	Cl	
28	CH ₂	H	H	H	H	NO ₂	H	OSO ₂ CH ₃	138.5-140

TABLE A (continued)

Cpd	X	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	m.p. (°C)
29	CH ₂	H	H	H	H	Cl	H	OSO ₂ CH ₃	112
30	CH ₂	H	H	H	H	CH ₃	H	OSO ₂ CH ₃	
31	CH ₂	-CH ₂ CH ₂ -		H	H	NO ₂	H	OSO ₂ CH ₃	
32	CH ₃ CH	H	H	H	H	Cl	H	OSO ₂ CH ₃	107
33	CH ₃ CH	H	H	H	H	NO ₂	H	OSO ₂ CH ₃	
34	CH ₃ CH	H	H	H	H	OSO ₂ CH ₃	H	Cl	
35	CH ₃ CH	H	H	H	H	Cl	H	OSO ₂ CF ₃	
36	CH ₃ CH	H	H	H	H	NO ₂	H	OSO ₂ CF ₃	
37	CH ₃ CH	H	H	H	H	NO ₂	H	NHSO ₂ CH ₃	
38	CH ₃ CH	H	H	H	H	Cl	H	NHSO ₂ CH ₃	
39	CH ₂	H	H	H	H	Cl	H	NHSO ₂ CH ₃	
40	CH ₂	H	H	H	H	NO ₂	H	NHSO ₂ CH ₃	
41	O	CH ₃	CH ₃	CH ₃	CH ₃	NO ₂	H	NHSO ₂ CH ₃	
42	O	CH ₃	CH ₃	CH ₃	CH ₃	Cl	H	NHSO ₂ CH ₃	
43	O	CH ₃	H	CH ₃	H	Cl	H	NHSO ₂ CH ₃	
44	O	CH ₃	H	CH ₃	H	NO ₂	H	NHSO ₂ CH ₃	
45	O	CH ₂ CH ₃	H	CH ₃	H	NO ₂	H	NHSO ₂ CH ₃	
46	CH ₃ CH	H	H	H	H	NO ₂	OCH ₃	OSO ₂ CH ₃	105
47	CH ₂	H	H	H	H	Cl	Cl	OSO ₂ CH ₃	160
48	(CH ₃) ₂ C	H	H	H	H	NO ₂	H	OSO ₂ CH ₃	178-180
49	CH ₂	H	H	H	H	NO ₂	H	OSO ₂ phenyl	157-158
50	CH ₂	CH ₃	CH ₃	H	H	NO ₂	H	OSO ₂ CH ₃	96-98
51	CH ₂	CH ₃	SCH ₃	H	H	NO ₂	H	OSO ₂ CH ₃	139-1405
52	CH ₂	CH ₃	SCH ₃	CH ₃	CH ₃	NO ₂	H	OSO ₂ CH ₃	sticky
53	CH ₂	CH ₃	CH ₃	CH ₃	CH ₃	NO ₂	H	OSO ₂ CH ₃	56-61
54	CH ₂	H	H	H	H	NO ₂	H	OSO ₂ C ₂ H ₅	103-105
55	CH ₂	CH ₃	CH ₃	H	H	NO ₂	H	OSO ₂ C ₂ H ₅	95-96
56	CH ₂	H	H	H	H	NO ₂	H	OSO ₂ iC ₃ H ₇	100-101
57	CH ₂	CH ₃	CH ₃	H	H	NO ₂	H	OSO ₂ iC ₃ H ₇	98-100
58	CH ₂	CH ₃	SCH ₃	H	H	NO ₂	H	OSO ₂ C ₂ H ₅	110-111
59	CH ₂	CH ₃	SCH ₃	H	H	NO ₂	H	OSO ₂ iC ₃ H ₇	115-116

Especially good activity has been demonstrated by Compound Nos. 28, 50, 53, 54 and 55.

The starting compounds, e.g. the compounds of formula II herein are known or, in cases where they are novel, can be produced by methods analogous to known methods or by methods described herein.

Thus, the enol esters of formula III can be prepared by the reaction of a 3,5-dione of formula II with a benzoyl halide of formula IV (wherein Q is a halogen atom) in the presence of a moderate base such as triethylamine.

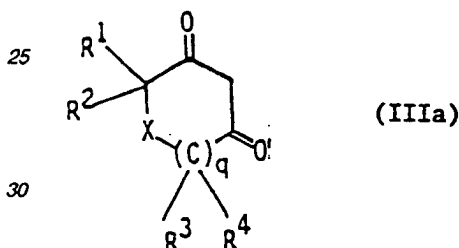


(III)

(IV)

Cycloalkanediones of formula III are known in the art or can be prepared according to procedures that are analogous to known procedures.

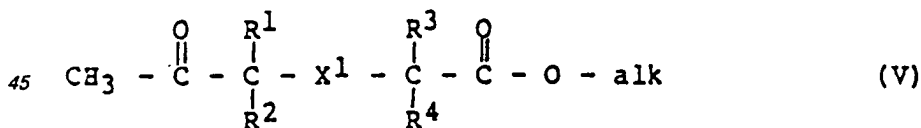
In particular, cycloalkanediones of formula IIIa



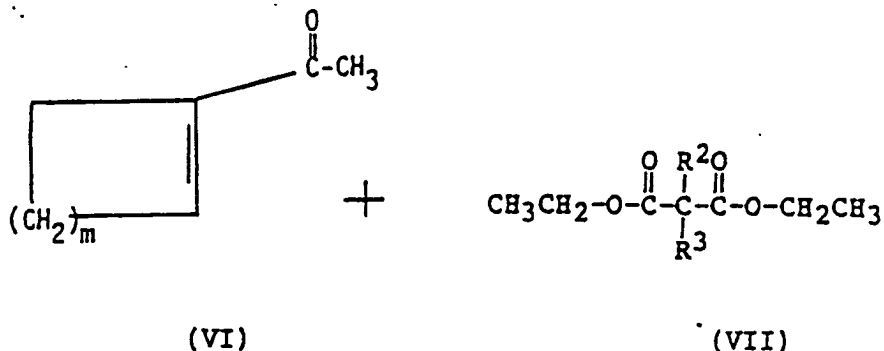
where X is CR₁'R₂' are known in the art.

2H-Pyran-3,5-(4H,6H)-diones of formula IIIa (where X is oxygen) can be synthesized by methods such as a) described by Morgan et al., JACS 79:422 (1957), or b) by treating a 2,5-substituted furanidine-3,4-dione (from Korobitsyna et al., J. Gen. Chem. USSR 27:1859 (1957)) with an alkyl diazoacetate, followed by heating in the presence of water.

The 2H-thiopyran-3,5-(4H,6H)-diones and piperidines of formula III (where X is sulfur or NR¹¹) can be synthesized by reacting a sulfide or sarcosinate of formula V (alk=methyl or ethyl and X¹=S or NR¹¹) with sodium methoxide.



The bicycloalkane diones of formula III can be prepared, for example, by reacting an acetylcycloalkene of formula VI (where m is zero to four) with a substituted diethyl malonate of formula VII to give a compound of formula III where q is one.



The acyl halides of formula IV can be prepared from the corresponding substituted benzoic acids according to the teaching of Reagents for Organic Synthesis, Vol. I, L.F. Fieser and M. Fieser (1967).

INTERMEDIATE COMPOUNDS

The following examples are presented to illustrate representative methods of preparing the intermediate compounds.

EXAMPLE 7

Boron trifluoride etherate (4.8 ml, 39.0 mmol) is added to a solution of 2,2,5,5-tetramethylfuranidine-3,4-dione (15.0 g, 78.0 mmol) in 20 ml of anhydrous ether. Ethyl diazoacetate (12.3 ml, 117.0 mmol) in 20 ml of ethyl ether is added at a rate such that nitrogen evolution does not become vigorous. The mixture is stirred at RT for 12 hours and is then quenched with water. The mixture is diluted with ether and washed with brine, then extracted with 5% K₂CO₃. The K₂CO₃ solution is washed with ether and neutralized with conc. HCl. The product is extracted with ether, dried and evaporated to give 4-carbethoxy-2,2,6,6-tetramethyl-2H-pyran-3,5-(4H,6H)-dione, a pink oil.

The above trione (5.11 g, 21.1 mmol) is dissolved in 25 ml of dimethyl sulfoxide, and water is added (0.8 ml, 42.2 mmol). The mixture is heated at 120° for 1 hour, or until gas evolution has ended. The reaction mixture is diluted with ether and washed with sat. NaCl. The solvent is removed and the crude product triturated with ether/hexane to give 2,2,6,6-tetramethyl-2H-pyran-3,5-(4H,6H)-dione, as white crystals.

EXAMPLE 8

To a solution of 4-hydroxy-3-methoxy-2-nitrobenzaldehyde (10.0 g, 50.7 mmol) in 200 ml of methylene chloride and containing triethylamine (10.60 ml, 1.5 eq.) at 0° is added methanesulfonyl chloride (4.32 ml, 6.39 g, 1.1 eq.) over a period of 5-10 min. The mixture is stirred for an additional 10 min., and is then washed with ice water, with dilute HCl, with sat. NaHCO₃ and with brine. The layers are separated and the organic layer is dried and evaporated to give 3-methoxy-4-methylsulfonyloxy-4-nitrobenzaldehyde.

The above aldehyde (13.25 g) is suspended in acetone and cooled to 0°. Jones reagent is added dropwise over approx. 15 min. until the solution is slightly orange, indicating an excess of the reagent. The reaction is stirred for approx. 1 hr., after which it is diluted with water and extracted with ethylacetate to give 3-methoxy-4-methylsulfonyloxy-2-nitrobenzoic acid.

EXAMPLE 9

3-Methoxy-4-methylsulfonyloxy-2-nitrobenzoic acid (5.13 g, 17.6 mmol) is heated under reflux with thionyl chloride for 2 hr., after which excess thionyl chloride is removed under vacuum. The resulting acid chloride residue is added to 2,2,6,6-tetramethyl-2H-pyran-3,5-(4H,6H)-dione (3.00 g, 17.6 mmol) dissolved in 50 ml of methylene chloride, with cooling to 5°, followed by dropwise addition of triethylamine (3.19 ml, 1.3 eq.). The mixture is stirred at RT for 2 hr. and then poured into water. The organic layer is washed with brine, dried and evaporated to give 2,2,6,6-tetramethyl-5-(3-methoxy-4-methylsulfonyloxy-2-nitrobenzoyl)-3,6-dihydro-2H-pyran-3-one.

EXAMPLE 10

EXAMPLE 10
To a solution of 2-chloro-4-hydroxybenzoic acid (3.45 g, 20 mmol) and sodium hydroxide (2.40 g, 60.0 mmol) in 30 ml of water is added, dropwise at 0°, methanesulfonyl chloride (2.57 ml, 3.80 g, 33.0 mmol). After addition is complete, the reaction mixture is stirred at RT for 30 min., after which it is poured into water, acidified with dil. HCl and extracted with ether. The combined organic extracts are washed with brine, dried and evaporated to give 2-chloro-4-methylsulfonyl-oxybenzoic acid.

EXAMPLE 11

To a solution of 5-methylcyclohexane-1,3-dione (1.79 g, 14.0 mmol) in 20 ml of methylene chloride containing triethylamine (2.90 ml, 20.8 mmol) is added, dropwise at 0°, a solution of 2-chloro-4-methylsulfonyl-

loxybenzoyl chloride, prepared from the corresponding acid (3.50 g, 14.0 mmol) and thionyl chloride, in methylene chloride (10 ml). After the addition is complete, the mixture is stirred for another 30 min. at 0°, after which it is diluted with methylene chloride, washed, dried and evaporated to dryness. The crude enol ester is treated with triethylamine (3.97 ml, 2 eq.) and acetone cyanohydrin (0.4 ml) in 25 ml of acetonitrile. After stirring overnight at RT, the reaction mixture is concentrated and poured into water. The combined organic extracts are washed with dilute HCl and with brine, dried and evaporated to dryness. The crude product is crystallized from ether to give 2-(2-chloro-4-methylsulfonyloxybenzoyl)-5-methyl-cyclohexane-1,3-dione.

EXAMPLE 12

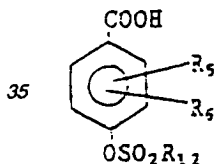
Sodium metal (2.31 g, 101.0 mmol) is dissolved in 50 ml of ethanol, and diethyl methylmalonate (17.6g, 101.0 mmol) is added, after which the mixture is stirred for approx. 30 min. under reflux. 1-Acetyl-1-cyclohexane (12.50 g, 101.0 mmol) is added and the mixture is stirred under reflux overnight. Potassium hydroxide (12.47 g, 222.2 mmol) dissolved in 40 ml of water is added and the mixture is heated under reflux for 4 hr. The ethanol is removed by rotary evaporation, and the residue is dissolved in water and washed with ether. The aqueous layer is acidified with conc. HCl and extracted with ether. The combined extracts are dried and the solvent is removed to give 4a,5,6,7,8,8a-hexahydro-4-methylnaphthalene-1,3(2H,4H)-dione.

To a mixture of the above dione (8.0 g, 44.4 mmol) and 2-chloro-4-methylsulfonyloxybenzoyl chloride (44.4 mmol) in 50 ml of methylene chloride is added, dropwise, triethylamine (8.04 ml, 1.3 equiv.), and the mixture is stirred at RT for 2 hr. The reaction mixture is diluted with methylene chloride, washed with water and evaporated to give 1-(2-chloro-4-methylsulfonyloxybenzoyloxy)-4a,5,6,7,8,8a-hexahydro-4-methyl-3(4H)-naphthalenone and 3-(2-chloro-4-methylsulfonyloxybenzoyloxy)-4a,5,6,7,8,8a-hexahydro-4-methyl-1(4H)-naphthalenone.

EXAMPLE 13

Following the procedure of Example 12, the sodium salt of diethyl malonate (161.0 mmol) and 1-acetyl-2-methyl-1-cyclopentene (20.0 g, 161.0 mmol) are reacted together to give 7a-methyl-2,3,7,7a-tetrahydro-1H-indene-4,6-(5H)-dione, which is then reacted with 2-chloro-4-methylsulfonyloxybenzoyl chloride (1 equiv.) to give 4-(2-chloro-4-methylsulfonyloxybenzoyloxy)-7a-methyl-2,3,7,7a-tetrahydro-1H-inden-6-one and 6-(2-chloro-4-methylsulfonyloxybenzoyloxy)-7a-methyl-2,3,7,7a-tetrahydro-1H-inden-4-one.

The following alkylsulfonyloxybenzoic acids, which are precursors of the alkylsulfonyloxybenzoyl halides that are within the scope of formula IV, are believed to be novel:

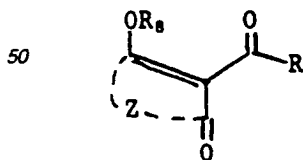


wherein,

R₅ is C₁₋₈alkyl, optionally substituted with one to six halogen atoms; C₁₋₈alkoxy, optionally substituted with one to six halogen atoms; (O)_nS(O)_nR₁₂; NR₁₂SO₂R₁₂; halogen; or nitro; R₆ is hydrogen or independently selected from the values of R₅; and R₁₂ is C₁₋₈alkyl, optionally substituted with one to six halogen atoms.

Claims

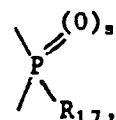
1. A compound of formula I



I

wherein

Z is a C₂-C₁₀ alkylene group, optionally substituted with one or more members selected from C₁₋₈alkyl, C₁₋₈alkoxy, C₁₋₈alkylthio, COOR₁₆, halogen; cyano; nitro; phenyl; R₈SO_n; benzyl; -NR₁₀R₁₁; R₁₂C(O)-; -SO₂NR₁₀R₁₁; and -N(R₁₀)C(O)R₁₁; said Z group further being optionally interposed by an oxygen atom, a group -S(O)_p-, a group



or a group $-N(R_{18})-$; and whereby two of any alkyl substituents may be joined to form a bicyclic; spiro or bridged alkylene ring;

R is phenyl or a 5- or 6-membered aromatic heterocycle containing one or two heteroatoms selected from oxygen, sulfur, and nitrogen; R being substituted by at least one member selected from the group consisting of $-OSO_2R_{12}$ and $-NR_{15}SO_2R_{12}$; R being optionally further substituted by one or two members selected from C_{1-8} alkyl, optionally substituted with one to six halogen atoms; C_{1-8} alkoxy, optionally substituted with one to six halogen atoms; phenyl; halogen; cyano; nitro; $-(O)_nS(O)_nR_9$; $-SO_2NR_{10}'R_{11}'$; $-N(R_{10}')C(O)R_{11}'$; or $-NR_{15}'SO_2R_{12}'$; whereby any two adjacent alkyl substituents may be joined to form a bicyclic alkylene ring;

R_8 is hydrogen; C_{1-8} alkyl; C_{1-8} alkylcarbonyl; C_{1-8} alkoxycarbonyl; C_{1-8} alkylsulfonyl; $C(O)NR_{13}R_{14}$; $P(O)(OR_{11})_2$; $R_{13}P(O)OR_{11}$; or a salt forming moiety;

R_9 and R_9' are independently phenyl; benzyl, or C_{1-8} alkyl, optionally substituted by one or more members selected from halogen, cyano, C_{1-2} alkoxy or C_{1-2} alkylthio;

R_{10} , R_{10}' , R_{11} , R_{11}' , R_{11}'' , R_{13} , R_{14} , R_{15} and R_{16} are independently hydrogen or C_{1-8} alkyl;

R_{12} is C_{1-8} alkyl, optionally substituted with one to six halogen atoms; or phenyl, optionally substituted with one to three members selected from C_{1-8} alkyl, C_{1-8} alkylcarbonyl, C_{1-8} alkoxycarbonyl, C_{1-8} alkylsulfonyl, $C(O)NR_{13}R_{14}$, $P(O)(OR_{11}')_2$ and $R_{13}P(O)OR_{11}''$;

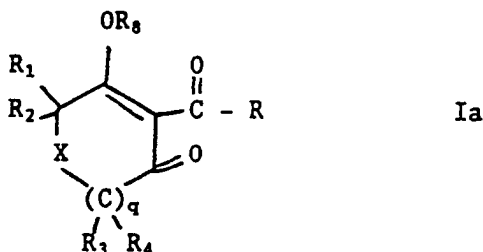
R_{17} is C_{1-8} alkyl or C_{1-8} alkoxy;

R_{18} is C_{1-8} alkyl;

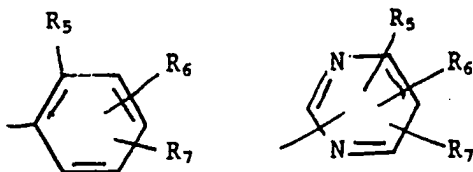
n , n' and p are 0, 1 or 2; and

s is 0 or 1.

2. A compound of formula Ia



wherein,
R is selected from the groups



X is oxygen, $S(O)_n$, $CR_1'R_2'$ or NR_{18} ;

R_1 , R_1' , R_2 , R_2' , R_3 , and R_4 are independently, hydrogen, C_{1-8} alkyl, C_{1-8} alkoxy, C_{1-8} alkylthio, or $COOR_{16}$; or R_1 and R_2 together form a C_{3-8} alkylene; or R_2 and R_2' together form a C_{1-4} alkylene optionally substituted with one to six C_{1-8} alkyl groups; or R_3 and R_4 together form a C_{3-8} alkylene;

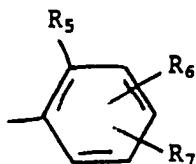
R_5 is C_{1-8} alkyl, optionally substituted with one to six halogen atoms; C_{1-8} alkoxy, optionally substituted with one to six halogen atoms; $-(O)_nS(O)_nR_{12}$; $-NR_{15}SO_2R_{12}$; halogen; cyano; or nitro;

each of R_6 and R_7 is independently hydrogen or selected from the values of R_5 ; with the proviso that at least one of R_5 , R_6 , and R_7 is a group $-OSO_2R_{12}$ or $-NR_{15}SO_2R_{12}$;

R_8 , R_{12} , R_{16} , R_{18} , n , and n' are as defined in claim 1; and

q is 0 or 1.

3. A compound according to claim 2 wherein R is the group



4. A compound according to claim 3 wherein X is oxygen or $CR_1'R_2'$, R_1' and R_2' are independently hydrogen or C_{1-4} alkyl, and q is one.

5. A compound according to claim 4 wherein R_1 , R_2 , R_3 , and R_4 are independently hydrogen, C_{1-4} alkyl, or C_{1-4} alkylthio.

6. A compound according to claim 5 wherein R_5 is selected from nitro, halogen, C_{1-4} alkyl, and C_{1-3} alkylsulfonyloxy, C_{1-3} alkylsulfonyl, and R_6 is selected from halogen, C_{1-4} alkoxy, halogen, and C_{1-3} alkylsulfonyloxy, and R_7 is selected from halo, C_{1-3} alkylsulfonyloxy, phenylsulfonyloxy, and $NHSO_2C_{1-4}$ alkyl.

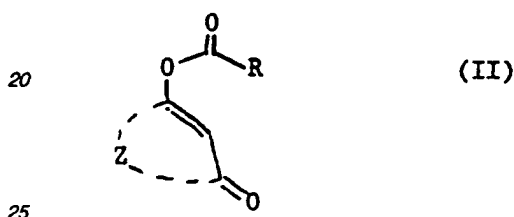
7. A method of controlling weeds comprising applying to the weeds or their locus an herbicidally effective amount of a compound of formula I as defined in claim 1.

8. A herbicidal composition comprising the compound of formula I as defined in claim 1, in association with an agriculturally acceptable carrier.

9. A method of controlling acari comprising applying to the acari or their locus an acaricidally effective amount of a compound of formula I as defined in claim 1.

10. A acaricidal composition comprising the compound of formula I as defined in claim 1, in association with a carrier.

11. A process of preparing a compound of formula I, stated in claim 1, which comprises reacting an enol ester of formula II

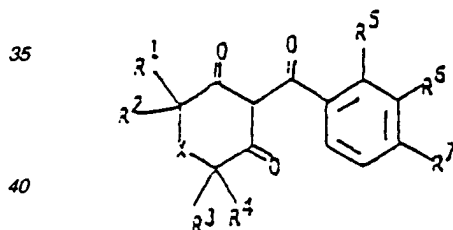


wherein R and Z are as defined in claim 1, with a cyanide source and a moderate base to obtain the compound of formula I where R_8 is hydrogen, followed, where desired, by etherification or esterification to the corresponding enol ethers or enol esters.

12. A process according to claim 11, substantially as described herein by way of Example.

13. A compound of formula I, whenever obtained by a process according to claims 11 or 12.

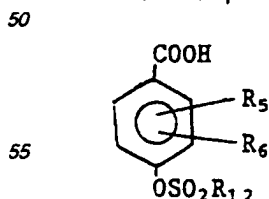
14. A compound of the formula



wherein

45 X is CH_2 , R_1 is H, R_2 is H, R_3 is H, R_4 is H, R_5 is NO_2 , R_6 is H, and R_7 is OSO_2CH_3 ; or
 X is CH_2 , R_1 is CH_3 , R_2 is CH_3 , R_3 is H, R_4 is H, R_5 is NO_2 , R_6 is H, and R_7 is OSO_2CH_3 ; or
 X is CH_2 , R_1 is CH_3 , R_2 is CH_3 , R_3 is CH_3 , R_4 is CH_3 , R_5 is NO_2 , R_6 is H, and R_7 is OSO_2CH_3 ; or
 X is CH_2 , R_1 is H, R_2 is H, R_3 is H, R_4 is H, R_5 is NO_2 , R_6 is H, and R_7 is $OSO_2C_2H_5$; or
 X is CH_2 , R_1 is CH_3 , R_2 is CH_3 , R_3 is H, R_4 is H, R_5 is NO_2 , R_6 is H, and R_7 is $OSO_2C_2H_5$.

15. A compound of the following formula:



wherein,

60 R_5 is C_{1-8} alkyl, optionally substituted with one to six halogen atoms; C_{1-8} alkoxy, optionally substituted with one to six halogen atoms; $(O)_nS(O)_nR_{12}$; $NR_{15}SO_2R_{12}$; halogen; or nitro;

R_6 is hydrogen or independently selected from the values of R_5 ; and

R_{12} is C_{1-8} alkyl, optionally substituted with one to six halogen atoms.

65